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PHYSICAL PROPERTIES OF PLASMA DEPOSITED SILICON NITRIDE LAYERS[1]

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This paper reports on the properties of PECVD silicon nitride. Ellipsometric data, the Auger depth analysis, IR data and stress measurements of the films are presented. The refractive index of films may be used to estimate the silicon content in the films.

I. INTRODUCTION

Silicon nitride layers deposited at low temperature by the PECVD method (a-SiN:H) are widely investigated for their application in VLSI circuits. They show excellent characteristcs as diffusion masks and passivation coatings. In addition, they present very high resistivity and dielectric constant [1]. In the PECVD technique using silane and ammonia as reactants, it is well established that the physical and electrical properties of the films are strongly influenced by the deposition conditions, i.e. the flow ratio of reactants, total pressure, substrate temperature, RF power and even the reactor geometry. Due to this fact it is difficult to compare the results in literature. Because the stoichiometry can be easily varied by varying the deposition conditions and because the stoichiometry affects the physical and electrical properties of the film, it is important to measure and correlate the various chemical, electrical and physical properties of these films. A property that is easy to measure and often correlated is the refractive index (RI). It has been shown that the RI depends on the Si/N atomic ratio of the a-SiN:H [2]. From the IR spectrum it is possible to determine the Si-H, N-H and the total hydrogen content [3]. The RI of a-SiN:H has been shown to be proportional to the Si-H/Si-N ratio [4,5].

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II. EXPERIMENTAL PROCEDURE

Films were deposited in a high frequency (13.56 MHz) parallel-plate plasma reactor. The gas flow into the reactor chamber was controlled by Brooks rotameters. Pure silane and ammonia were used as reactants for these deposition processes. The feed gas was introduced into the reaction volume through a shower on the upper electrode. After passing the substrates the gases flowed down along the reactor wall and were exhausted through a pumping port in the bottom part of the reactor. The diameters of upper and lower electrodes were 155 and 210 mm, respectively, and were 30 mm apart. The system was evacuated by a LN_2 cold-trapped diffusion pump to a base pressure of $2x10^{-3}$ Pa before the gas flow was started. The pressure during the deposition was kept constant at 80 Pa. At this pressure the deposition rate was 25 nm/min and the layers thickness homogeneity was better than 3%.

The lower electrode on which the substrates were placed was grounded and heated by a resistance heater, where its temperature was monitored by an embedded thermocouple. The upper electrode was driven by a capacitively coupled RF power supply through a matching network. Film thickness and refractive index were measured by means of a He-Ne laser ellipsometer (λ=632.8 nm). Fourier transform infrared (FTIR) spectroscopy studies were performed with 500 nm thick silicon nitride deposited on bare silicon substrates. Auger analyses for compositional depth profiles were performed with 100 nm thick films on GaAs substrate surfaces. For stress measurements the newtonian interefence technique was used.

III. RESULTS AND DISCUSSION

Infrared analysis of a-SiN:H films (T_d = 300°C, Φ_{SiH_4} = 10 sccm, Φ_{NH_3} = 50 sccm) shows the presence of N-H (3360 cm^{-1}), Si-H (2160 cm^{-1}), Si-O (1170 cm^{-1}), Si-N (830 cm^{-1}) bonds (Fig. 1). Thus hydrogen in a-SiN:H exists only in the form of N-H and Si-H bonds, because no O-H bond was observed.

The Si-H is more sensitive to thermal heating as compared to the N-H bonds. As a-SiN:H are annealed at a temperature above the deposition one the Si-H bonds are generally broken first and hydrogen is released out from the film. In the Fig. 1 we can see that with the increasing RF power the amount of hydrogen bonded in the form of Si-H decreases. This can be explained by the fact that the increase of energy of impinging ions leads to the dissociation of weaker Si-H bonds as compared with N-H bonds. Simultaneously the additional heating of substrates occurs due to this additional bombardment, which also increases the release of bonded hydrogen. Both Si-H and N-H peaks disappeared after 20 minutes of annealing in forming gas at 860°C. This annealing is often used in GaAs technology, where a-SiN:H films are succesfully used as a protective material to prevent As diffusion from the GaAs

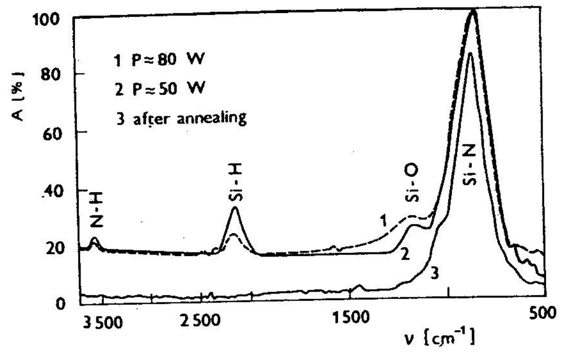

Fig. 1. IR spectrum of a-SiN:H.

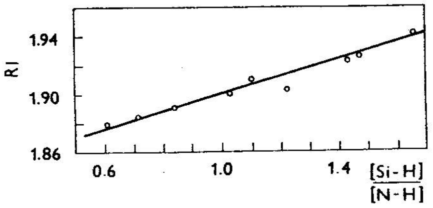

Fig. 2. Refractive index vs. Si-H/N-H ratio.

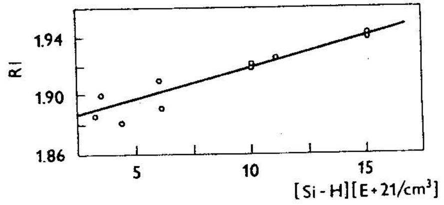

Fig. 3. Refractive index vs. Si-H content.

substrates during the postimplantation high temperature annealing. Fig. 2 shows the refractive index as a function of the Si-H/N-H ratio determined from the FTIR analysis of the films. Fig. 3 is a plot of RI as a function of the Si-H content for ten films. Since the Si-H content as measured by IR analysis is proportional to the Si content of the film [8] and since the RI is proportional to the Si-H content, it is concluded that RI of the films is largely determined by the Si content in the film.

The Auger depth profile analysis results for plasma deposited Si-rich silicon nitride are shown in Table 1 and the representative Auger depth profile is shown in Fig. 4.

The sample No. 1. has higher RI than the sample No. 2 at almost the same value of Si/N. This is caused by the fact that the sample No. 2. has more bonded oxygen, so it is closer with its composition to the SiO_2 with RI=1.45.

Auger depth profiles analyses of all films show poor compositional uniformity during the first 20 nm of deposition for all experimental films examined. The bottom layer near the substrate interface is richer in silicon than the top layer. These

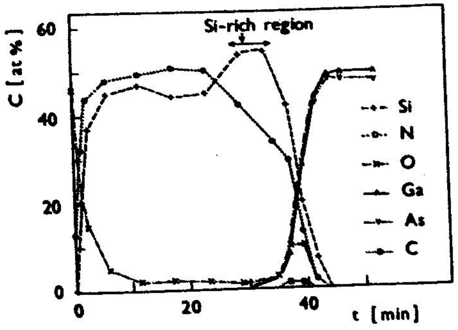

Fig. 4. AES depth profile for a-SiN:H film.

Table 1

Bulk compositions of Si-rich a-SiNH films by AES (at.%).

N°	RI	Si	N	O	Stoichiometry	Si/N
1	2.153	45	54	0.5	$Si_3N_{3.6}$	0.83
2	1.979	45	53	2	$Si_3N_{3.5}$	0.85
3	2.023	48	50	2	$Si_3N_{3.1}$	0.96
4	2.050	50	48	2	$Si_3N_{2.8}$	1.04
Stoichiometric Si_3N_4		43	57	0	Si_3N_4	0.75

two layer structures are probably a result of the changes in the electron temperature and the density of a silane reactive species concentration during the process, i.e. the initial transient changes in radio frequency power and gas impedances [7]. Due to the weaker Si-H bonds of silane as compared to the N-H bonds of ammonia more silane is broken into reactive species during the initial transient periods. This will substantially increase the concentration ratio of the Si/N reactive species during initial transient periods compared to those of steady state plasma. Therefore more silicon will be deposited on the substrate during this period thus creating the silicon-rich interface phenomena in all a-SiN:H films.

The mechanical stress in the substrate/film system across the film thickness and the substrate manifests itself in the form of bending. If the stress is too high, the film induces defects in the substrate material or tends to peel off. The mechanical stress was determined by measuring the curvature of silicon strips coated with the a-SiN:H films. The radii of curvature were determined before and after

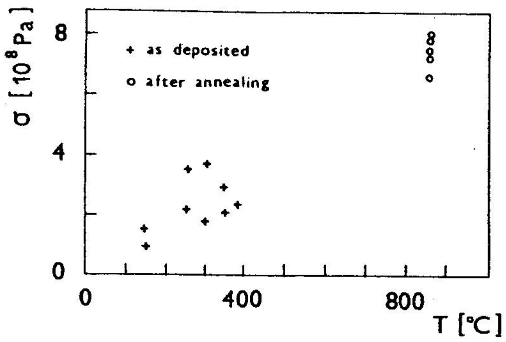

Fig. 5. Influence of deposition temperature on the stress.

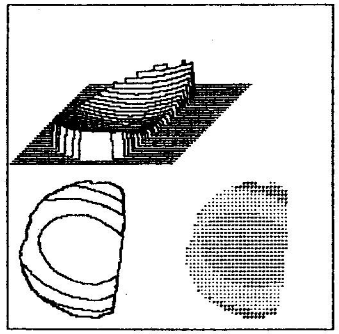

Fig. 6. Measured profile of surface after annealing.

deposition of each type of film as well as after high temperature annealing. The value of the radius was used for the evaluation of the average film stress according to the formula [6]:

$$\sigma = \frac{E_s t^2}{6\ T}\left(\frac{1}{R} - \frac{1}{r}\right) \qquad (1)$$

where E_S is the elastic modulus of the silicon substrate ($1.7\text{x}10^{11}\text{Nm}^{-2}$), t and T are the thicknesses of the substrate and the film, respectively and R and r are the radii of curvature with and without film, respectively.

The positive values of σ correspond to a tensile stress, the negative values of σ to a compressive stress. From Fig. 5 and Fig. 6 we can see that all deposited films have tensile mechanical stresses in the range from 0.5 to 4 Nm^{-2}. There was no obvious correlation between the deposition temperature and the resulting intrinsic stress. However, after high temperature annealing we observed an increase in stress up to $8\text{x}10^8$ Nm^{-2}. The tensile stress of films can be explained by a hydrogen desorption rate which is low compared to the rate at which radicals formed in the gas phase are inserted into Si-H and N-H bonds. This leads to a top layer with a relatively high hydrogen content. Owing to high temperatures, hydrogen desorption and cross-linking do not stop after the actual deposition step but continue for a while leading to a layer which shrinks at a deposition temperature. This automatically leads to a tensile stress in the layer. As we can see in Fig. 1. the Si-H and N-H peaks dissapeared after annealing. Thus it is obvious that there exists the correlation between the intrinsic stress of a-SiN:H layers and the amount of bonded hydrogen in it. These results are in good agreement with others reported elsewhere [9,10,11,12].

IV. CONCLUSION

The physical properties of a-SiN:H films deposited from pure SiH_4 and NH_3 at a frequency of 13.56 MHz have been determined. IR analyses show that the films deposited under the described conditions contain significant amounts of hydrogen. Substantial loss of hydrogen was observed after annealing. Although elipsometer measurements showed that film thickness and RI uniformity are good, Auger depth profiles revealed poor compositional uniformity during the first 20 nm deposition. The elemental composition expressed as Si/N ranges from 0.75 to 1.04. The amount of bonded hydrogen decreased with increasing RF power. Films with less hydrogen content have a greater tensile stress.

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ФИЗИЧЕСКИЕ СВОЙСТВА СЛОЕВ НИТРИДА КРЕМНИЯ НАПИЛЕННЫХ В ПЛАЗМЕ

Приводятся свойства PECVD тонкого слоя нитрида кремния полученные на основании элипсометрических данных, глубинного анализа Оже, инфракрасных данных и измерения прочности. Индекс преломления используется в оценке содержания кремния в пленках.